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# PATENT SPECIFICATION

NO DRAWINGS

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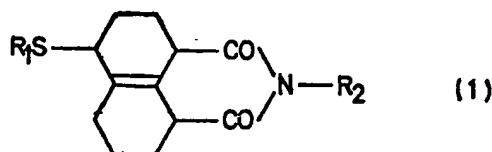
## COMPLETE SPECIFICATION

### Naphthalimide Derivatives and a method for their Manufacture

We, MITSUBISHI CHEMICAL INDUSTRIES LIMITED, a Japanese Company, of 4, 2-chome, Marunouchi, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 The invention relates to new naphthalimide derivatives and to a method for their manufacture.

The new naphthalimide derivatives provided according to the invention have the following formula (1):



10 wherein R<sub>1</sub> denotes an unsubstituted or substituted alkyl, aryl, aralkyl or cycloalkyl group having no dyestuff character and R<sub>2</sub> denotes a hydrogen atom or an unsubstituted or substituted alkyl, aryl, aralkyl or cycloalkyl group having no dyestuff character.

15 The naphthalimide derivatives are optical whitening agents for various synthetic organic materials of high molecular weight. The compounds when dissolved or dispersed in a suitable liquid medium or when applied to a suitable material emit a distinctive greenish blue fluorescence in daylight or ultraviolet rays showing a wide absorption in the ultraviolet range. Further, the compounds generally have good stability and exhibit good affinity with synthetic organic high molecular weight materials. The compounds of formula (1) thus have a durable optical whitening effect on the synthetic materials of high molecular weight.

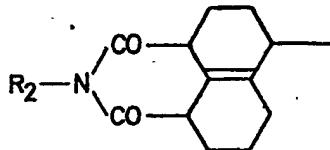
20 The preferred naphthalimide derivatives include N-alkyl-4-alkylthio-naphthalimides, N - hydroxyalkyl - 4 - alkylthio - naphthalimides, 4 - alkylthionaphthalimides, N - aryl - 4 - alkylthio - naphthalimides, N - (N',N' - dialkylaminoalkyl)-4 - alkylthio - naphthalimides, N - alkyl - 4 - hydroxyalkylthio - naphthalimides, N - alkyl - 4 (N',N' - dialkylamino - alkylthio) - naphthalimides and N - alkyl - 4 - arylthio-naphthalimides. R<sub>1</sub> in the formula (1) may, for example, be a methyl, ethyl, n- or iso-propyl, n- or iso-butyl, n- or iso-pentyl, n- or iso-hexyl, n-octyl, 2-ethylhexyl, n- or iso-dodecyl, or n- or iso-tridecyl group. Further R<sub>1</sub> may be a substituted alkyl group containing a hydroxy, alkoxy, aryl, primary amino secondary amino such as alkylamino, tertiary amino such as bisalkylamino or quaternary ammonium, such as trialkylammonium, group. Thus R<sub>1</sub> may, for example, be a hydroxyethyl, hydroxypropyl, hydroxybutyl, methoxyethyl, ethoxyethyl, ethoxypropyl, propoxypropyl, benzyl, aminoethyl, aminopropyl, N,N-dimethylaminoethyl, N,N-dimethylaminopropyl,

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5 N-trimethylammonium ethyl, N-trimethylammonium propyl, N-triethylammonium ethyl or N-triethylammonium propyl group. Still further, R<sub>1</sub> may be an aryl group such as phenyl or naphthyl or a substituted aryl group substituted by an alkyl, amino, secondary aminoalkyl, tertiary amino alkyl, quaternary ammonium alkyl, or nitro group or by a halogen atom. Still further, R<sub>1</sub> may be cycloaliphatic group such as cyclohexyl. Also R<sub>1</sub> may, for example, be a substituted aryl group as is shown in the formula:

5



10 R<sub>2</sub> in the formula (1) denotes either a hydrogen atom or an unsubstituted or substituted alkyl, aryl, aralkyl or cycloalkyl group having no dyestuff character and which may be one of the several groups given by way of example in relation to R<sub>1</sub>.

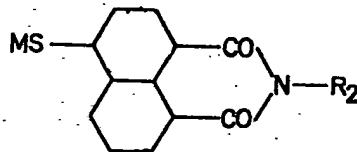
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Specific examples of the new compounds are given in the Examples.

The most practical method for manufacturing the new compounds comprises etherifying 4-mercapto-naphthalimide or a derivative thereof having the following formula:

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wherein M denotes a hydrogen or alkali metal atom, for example sodium or potassium, and R<sub>2</sub> is of the same significance as in formula (1), by the use of an etherifying agent having no dyestuff character.

20 Suitable etherifying agents to be used for etherifying the 4-mercapto-naphthalimides include, strong acid esters, for example, alkyl sulphates such as dimethyl sulphate or diethyl sulphate; organic compounds containing an active halogen atom, for example, alkyl halides such as methyl iodide, ethyl iodide, methyl bromide, ethyl bromide, butyl bromide, methyl chloride, and ethyl chloride, substituted alkyl halides such as ethylene chlorohydrin, 1-N,N-dimethylamino-2-chloroethane and benzyl chloride, and halogenated aryl derivatives such as p-nitrochlorobenzene and 4-chloro-N-methyl-naphthalimide; and esters of organic sulphonic acids such as the methyl and ethyl esters of p-tolene sulphonic acid. The etherification reaction may be 25 efficiently performed in the presence of an alkaline substance, preferably an alkali metal hydroxide, alkali metal carbonate, alkali metal bicarbonate, alkali metal phosphate, alkali metal silicate or alkali metal acetate. The etherification reaction is effected generally at a temperature in the range from about 20 to 200°C while preferably using an inert diluent such as water or an alcohol. Generally, the reaction product a compound of formula (1), is allowed to precipitate at room temperature and subsequently separated by filtering. Alternatively, the reaction liquor is either acidified or concentrated by distilling the diluent off the reaction liquor so that the reaction product is 30 precipitated and then separated by filtration. The purity of the reaction product thus obtained is generally high enough but the purity may be enhanced, if required, either by washing the said reaction product employing an alkaline aqueous solution or by recrystallization of the said reaction product employing a solvent.

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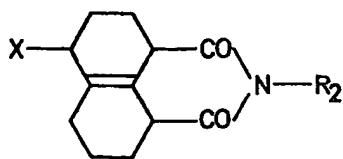
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35 The 4-mercapto-naphthalimides employed as the starting materials in the above-mentioned methods may be manufactured in an advantageous manner by a method in which 4-halogeno-naphthalimides of the following formula:

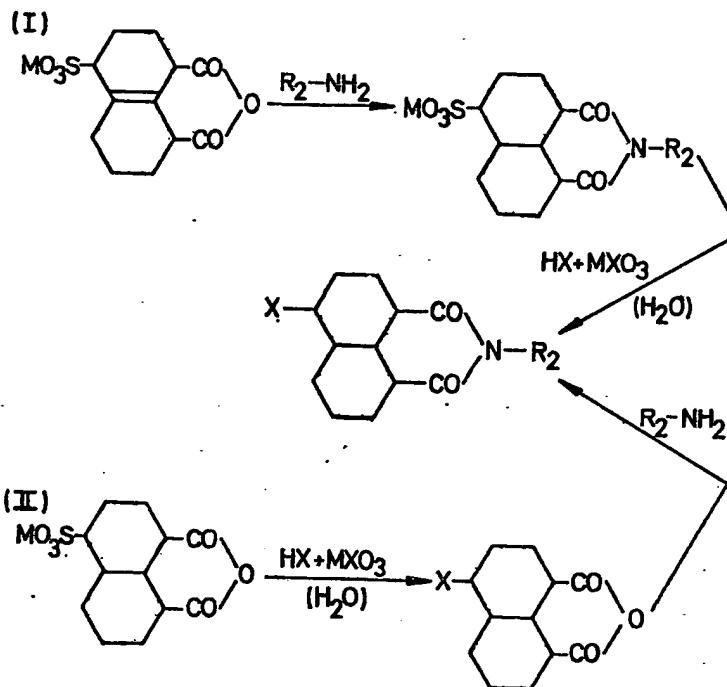


wherein X denotes a halogen atom and R<sub>2</sub> has the same significance as in formula (1), are caused to react with an alkali metal sulphide of the formula M<sub>2</sub>SY, M denoting an alkali metal and y a number from 1 to 5, in the presence of an inert solvent such as water or an alcohol or an aqueous alcohol at a temperature from 30 to 100°C.

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The aforementioned 4-halogeno-naphthalimides may themselves be manufactured in an economical manner in accordance with either of the two processes shown by the following reaction schemes:

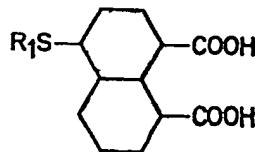


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wherein M denotes a hydrogen or an alkali metal atom and X a halogen atom.

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The compounds of formula (1) may also be manufactured by condensing a compound of the formula:



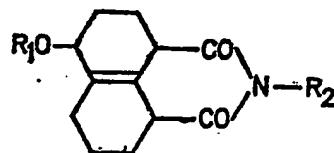
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wherein R<sub>1</sub> is of the same significance as in formula (1) or an anhydride thereof, with a compound of the formula R<sub>2</sub>-NH<sub>2</sub>, R<sub>2</sub> having the same significance as in formula (1).

The compounds of formula (1) exert a remarkable whitening effect on various materials, particularly on synthetic organic high molecular weight materials by fixing, penetrating, mingling, or adhering.

The treatment of a polyester textile material such as polyethylene terephthalate is generally performed in accordance with conventional methods for dyeing this textile material by using an aqueous dispersing medium containing one of the compounds of the invention. For this purpose, a treating bath is made up by uniformly dispersing the compound in water by the use of a suitable dispersing agent and/or a wetting agent, the said bath being used for dipping or padding the polyester textile material at a temperature up to 100°C. In some cases, the so-called carrier dyeing method may be carried out wherein a "carrier" such as chlorobenzene is employed. Also the so-called high temperature dyeing or thermosol process to be employed for dyeing polyester textile material is applicable as the method of treatment according to the invention. Polyester textile material thus treated emits greenish blue fluorescence in daylight or ultraviolet rays. Hence, a remarkable whitening effect is imparted while neutralizing the yellowish tint of the textile material. The new compounds may be efficiently applied to various types of synthetic textile materials including polyvinyl materials such as polyacrylonitrile and polyvinyl chloride; nitrogen-containing textile materials such as polyamides, polyolefin textile materials, such as polypropylene; and cellulose esters such as cellulose acetate. The new compounds according to the invention may also be used to whiten various synthetic resins in film, sheet, plate, board, tube, pipe, block, or other moulded form. For example, mixing a compound according to the invention with polystyrene or polymethyl methacrylate followed by extrusion or injection moulding results in a transparent moulded material which emits greenish blue fluorescence. A brilliant, coloured material may be obtained by blending a suitable colouring agent in the abovementioned mixing. The new compounds may also be applied to white-enhancing treatment of various moulded materials composed of synthetic resins such as polyvinyl chloride, polyacrylates, polyesters, polycarbonates, polyurethanes, polyamides, and polyolefins. As a result of such treatment an excellent white-enhancing effect is always obtained. The new compounds of the invention may be employed in a mixture with an optical whitening agent having the formula:



wherein R<sub>1</sub> and R<sub>2</sub> each are of the same significance as in formula (1). Such a mixture gives an optical whitening effect which emits fluorescence having a more bluish tint. The white-enhancing treatments with the compounds according to the invention may be carried out by methods other than those described. For example, the compounds according to the invention may be mixed in a suitable step during the process of manufacturing the textile material or synthetic resin. Further, the surfaces of moulding articles may be coated with a suitable solvent containing one of the new compounds. The invention is illustrated in the following examples in which the term "part" denotes part by weight unless otherwise specified. The melting point of the compounds shown in the following examples is an uncorrected value.

**EXAMPLE 1.**  
24.6 parts of N-methyl-4-chloro-naphthalimide were added to a solution consisting of 15.6 parts of sodium sulphide (Na<sub>2</sub>S), 100 parts of water and 200 parts of methanol, and heated, with stirring to effect reaction, for 4 hours at the boiling point. Upon completion of the reaction the reaction liquor was cooled to about 50°C, a solution composed of 20.8 parts of sodium bisulphite and 40 parts of water was added, followed by filtration to remove the precipitate. The filtrate was acidified by adding thereto a quantity of dil. HCl, filtered to remove the precipitate, rinsed with cold water until the precipitate becomes neutral, and dried under reduced pressure. Thus 19.5 parts of N-methyl-4-mercapto-naphthalimide of melting point from 214.5 to 216.2°C were obtained. The analytical values of this product closely approximate to the calculated values as indicated below:

	C(%)	H(%)	N(%)	S(%)
Calcd. for $C_{13}H_9NO_2S$	64.18	3.73	5.77	13.17
Found	60.94	3.37	6.20	13.28

The same product was obtained by using N-methyl-4-bromo-naphthalimide in place of N-methyl-4-chloro-naphthalimide. The same product was also obtained by use of the sodium polysulphides  $Na_2S_2$ ,  $Na_2S_3$ ,  $Na_2S_4$  and  $Na_2S_5$  in place of sodium sulphide ( $Na_2S$ ). 5

**EXAMPLE 2.**

24.6 parts of N-methyl-4-chloro-naphthalimide were added to a solution containing 18.8 parts of a mixture of sodium sulphide ( $Na_2S$ ) and sodium disulphide ( $Na_2S_2$ ) in 300 parts of water and heated with stirring to effect reaction for ten hours at a temperature from 95 to 98°C. Upon completion of the reaction, the product was subjected to the same treatment as in Example 1 to yield 19.0 parts of N-methyl-4-mercaptop-naphthalimide. 10

**EXAMPLE 3.**

28.8 parts of N-n-butyl-4-chloro-naphthalimide were added to a solution comprising 22.0 parts of sodium disulphide, 110 c.c. of water and 200 parts of ethanol and heated with stirring to effect reaction for 4 hours at the boiling point. Upon completion of the reaction, 250 parts of water were added to the reaction mixture followed by a solution comprising 20.8 parts of sodium bisulphite and 40 parts of water, and the precipitate was filtered off. The filtrate contained 20.0 parts of sodium salt of N-n-butyl-4-mercaptop-naphthalimide. The filtrate was subjected to the same treatment as in Example 1 to yield 14.3 parts of N-n-butyl-4-mercaptop-naphthalimide of melting point from 116.5 to 118.0°C. The same product was obtained by employing N-n-butyl-4-bromo-naphthalimide in place of N-n-butyl-4-chloro-naphthalimide. The analytical values of this product closely approximate to the calculated values as indicated below: 15

	C(%)	H(%)	N(%)	S(%)
Calcd. for $C_{18}H_{15}NO_2S$	67.34	5.27	4.91	11.22
Found	66.60	5.25	4.88	11.27

**EXAMPLE 4.**

12.0 parts of sodium hydroxide and 26.5 parts of a sodium salt of N-methyl-4-mercaptop-naphthalimide manufactured in accordance with the method of Example 1 or 2 were dissolved in 500 parts of water. To the resulting solution were added 25.2 parts of dimethyl sulphate and the mixture was stirred for 10 hours at a temperature from 20 to 30°C. Upon completion of the reaction, the reaction mixture was filtered to remove the precipitate. The filtered cake was rinsed in succession with aqueous sodium carbonate solution and water until the cake was neutral, and dried to yield N-methyl-4-methylthio-naphthalimide in theoretical yield. Recrystallization of this product from acetic acid yielded a purified product of melting point from 219.5 to 220.0°C. The analytical values of this product closely approximate to the calculated values as shown below: 30

	C(%)	H(%)	N(%)	S(%)
Calcd. for $C_{14}H_{11}NO_2S$	65.3	4.29	5.45	12.45
Found	63.98	4.21	5.30	12.10

The same product was obtained by use of (i) 15.9 parts of sodium carbonate and (ii) 20.7 parts of potassium carbonate in place of the 12.0 parts of sodium hydroxide.

This product emits distinct fluorescence of greenish blue tint in such organic solvents as methanol or acetic acid. Further, this product gives an excellent optical white-enhancing effect to organic high molecular weight materials.

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**EXAMPLE 5.**

12.0 parts of sodium hydroxide were dissolved in a solution containing 26.5 parts of sodium salt of N-methyl-4-mercaptop-naphthalimide manufactured by the method in Example 1 or 2 and 500 parts of water, 37.2 parts of methyl ester of p-toluene sulphonic acid were added thereto, and the mixture was stirred for 2 hours at a temperature from 20 to 30°C and subsequently for 2 hours at 80°C. Upon completion of reaction, the reaction product was cooled and the precipitate filtered off washed with water and dried to give in theoretical yield N-methyl-4-methylthio-naphthalimide of the same grade as in Example 4.

10

**EXAMPLE 6.**

12.0 parts of sodium hydroxide were dissolved in an aqueous solution comprising 26.5 parts of sodium salt of N-methyl-4-mercaptop-naphthalimide manufactured by the method of Example 1 or 2 to which 41.2 parts of n-butyl iodide were added and heated to cause reaction for 2 hours at 85°C. Upon completion of the reaction, the reaction product was cooled and the precipitate filtered off. The filter cake was rinsed in succession with methanol and water, and dried to give in theoretical yield N-methyl-4-n-butylthio-naphthalimide. The recrystallization of this product from acetic acid gave a pure product of melting point from 101.0 to 102.5°C. This material emits a distinctive fluorescence of greenish blue in methanol or acetic acid, and imparts an excellent optical white-enhancing effect to organic high molecular weight materials.

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**EXAMPLE 7.**

30.7 parts of sodium salt of N-n-butyl-4-mercaptop-naphthalimide manufactured by the method in Example 3 and 12.0 parts of sodium hydroxide were dissolved in 500 parts of water to which 25.2 parts of dimethyl sulphate were added, and the mixture was stirred for 10 hours at a temperature from 30 to 40°C. Upon completion of the reaction, the reaction mixture was subjected to the same treatment as in Example 4 to give in theoretical yield N-n-butyl-4-methylthio-naphthalimide of melting point above 330°C. This material emits a remarkable fluorescence in methanol or acetic acid, and imparts an excellent optical white-enhancing effect to various kinds of organic materials.

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**EXAMPLE 8.**

To a solution comprising 400 parts of water and 100 parts of methanol were added 29.5 parts of sodium salt of N-(2'-hydroxyethyl)-4-mercaptop-naphthalimide (which is obtained by reacting N-(2'-hydroxyethyl)-4-chloro-naphthalimide with sodium sulphide in accordance with Example 2) and 12.0 parts of sodium hydroxide. 50.4 parts of dimethyl sulphate were added to the resultant solution, which was stirred for 5 hours at a temperature from 20 to 30°C, and caused to react for 4 hours at 85°C. Upon completion of the reaction, the reaction mixture was subjected to the same treatment as in Example 4 to give in theoretical yield N-(2'-hydroxyethyl)-4-methylthio-naphthalimide of melting point from 176.8 to 177.2°C.

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The analytical values of this product closely approximate to the calculated values as shown below:

	C(%)	H(%)	N(%)	S(%)
Calcd. for C <sub>15</sub> H <sub>18</sub> NO <sub>3</sub> S	62.75	4.53	4.88	11.15
Found	62.00	4.50	4.92	11.13

50 This material emits a remarkable fluorescence in organic solvent, and imparts an excellent optical white-enhancing effect to various kinds of organic materials.

50

## EXAMPLES 9 TO 11.

5 An etherifying agent and a starting mercapto-naphthalimide compound listed respectively in columns A and B of the following table were reacted in accordance with the method described in Example 4 to yield a novel optical whitening agent correspondingly listed in column C.

5

	A	B	C	
			product	melting point
EX.9	dimethyl sulphate	sodium salt of 4-mercaptop-naphthalimide	4-methylthio-naphthalimide	285.2—288.8°C.
EX.10	-ditto-	sodium salt of N-(N',N'-dimethylamino) propyl-4-mercaptop-naphthalimide	N-(N',N'-dimethylamino) propyl-4-methylthio-naphthalimide	196.0—201.5°C.
EX.11	-ditto-	sodium salt of N-phenyl-4-mercaptop-naphthalimide	N-phenyl-4-methylthio-naphthalimide	296.8—271.2°C.

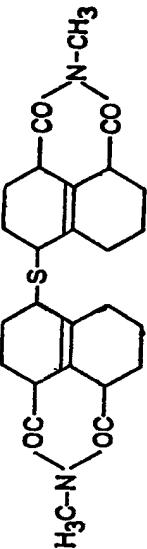
Note: In Examples 10 and 11, the reaction continued for 10 hours initiated at a temperature from 20 to 30°C followed by further reaction for 0.5 to 4 hours at a temperature from 85 to 95°C.

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## EXAMPLES 12 TO 16.

An etherifying agent and a starting mercapto-naphthalimide compound listed, respectively, in columns A and B were reacted in accordance with the method described in Example 6 to yield a novel optical whitening agent listed correspondingly in column C in the following table:

10

	A	B	C	melting point
		product		
EX.12	ethylene chloro- hydrin	sodium salt of N-methyl- 4-mercaptop- naphthalimide	N-methyl-4-(2'-hydroxy) ethylthio-naphthalimide	127.5— 131.5°C.
EX.13	2-(N,N- dimethyl- amino)- ethyl chloride benzyl- chloride	-ditto- -ditto- -ditto-	N-methyl-4-(N',N'-dimethyl- aminoethylthio)-naphthalimide N-methyl-4-benzylthio- naphthalimide	121.8— 124.0°C.
EX.14	p-nitro- chloro- benzene	sodium salt of N-methyl- 4-mercaptop- naphthalimide	N-methyl-4-(4'-nitro) phenylthio-naphthalimide	178.8— 179.5°C.
EX.15				237.5— 238.5°C.
EX.16	N-methyl 4-chloro- naphthal- imide	ditto -		299.0— 303.2°C.

Note: In Examples 15 and 16 the reaction continued for 8 hours at a temperature from 95 to 100°C.

## EXAMPLE 17.

5      1 part of N-methyl-4-methylthio-naphthalimide manufactured by the method in Example 4 was mixed with 2 parts of a dispersing agent which was a condensate of naphthalene-2-sulphonic acid with formaldehyde. The mixture was pulverized into an easily dispersible powder. The powder was dispersed in 30,000 parts of water to prepare a treatment bath. 150 parts of carrier (chlorobenzenes) were added to the bath in which 1,000 parts of polyester textile material were treated at a temperature from 98 to 100°C for 2 hr. The treated textile material was subjected to soaping in 10,000 parts of aqueous solution containing 30 parts of an anion surface active agent at 90°C for 15 min. and then rinsed and dried. The polyester textile material was invested with a remarkable whitening effect having good fastness. The same results as those in this example were obtained in cases where the compounds obtained by the methods in Examples 6 to 16 were used.

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15     1 part of N-methyl-4-methylthio-naphthalimide was mixed with 2 parts of a dispersing agent which was a condensate of 2-naphthol-6-sulphonic acid, cresol and formaldehyde. The mixture was pulverized into an easily dispersible powder. The powder was dispersed in 30,000 parts of water to prepare a treatment bath. In this bath were immersed 1,000 parts of polyester textile material to be subjected to a treatment at 120°C for 1.5 hr. The treated textile material was then subjected in sequence to soaping, rinsing, and drying as in Example 17. Thus a remarkably whitened polyester textile material was obtained. Any of the various compounds in Examples 6 to 16 may be used for performing the same treatment as in the present Example to obtain a similarly whitened polyester textile material as in this Example.

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20

25     1 part of N-methyl-4-methylthio-naphthalimide was dispersed in 30,000 parts of water to prepare a treatment bath as in Example 18. In the bath were immersed 1,000 parts of cellulose acetate textile material and the bath was maintained at 85°C for 1 hr. The treated textile material was then subjected to soaping at 50°C, rinsing and drying. Thus, the treated textile material is invested with a remarkable whitening effect. 1,000 parts of polyamide textile material and 1,000 parts of polyacrylonitrile textile material were similarly treated but at a bath temperature of 100°C. A similar whitening effect was produced. Further, the whitening of these textile materials was also effected with the compounds in Examples 6 to 16.

25

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35     A mixture of 1 parts of N-methyl-4-methylthio-naphthalimide and 2 parts of the dispersing agent employed in Example 18 was dispersed in 15,000 parts of water to prepare a treatment bath as in Example 18. In the bath were immersed 500 parts of a polypropylene textile material followed by heating at 98 to 100°C for 1.5 hr. and then soaping, rinsing, and drying. A remarkable whitening effect was thus imparted to the polypropylene textile material.

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45     A mixture of 0.01 part of N-methyl-4-methylthio-naphthalimide, 1 part of N-methyl-4-methoxy-naphthalimide and 2 parts of the dispersing agent employed in Example 17 was dispersed in 30,000 parts of water. 150 parts of carrier (chlorobenzenes) were added to the bath in which 1,000 parts of polyester textile material were treated at a temperature from 98 to 100°C for 2 hr. The treated material was then subjected in sequence to soaping, rinsing, and drying as in Example 17. The polyester textile material was invested with a remarkable whitening effect having good fastness.

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50     EXAMPLE 22.

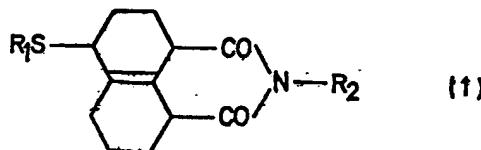
55     A mixture of 2 parts of N-methyl-4-methylthio-naphthalimide and 10,000 parts of polystyrene resin pellets was kneaded at 190—200°C, and then moulded into a plate using an injector. A transparent plate was obtained which emits an outstanding blue fluorescence. By adding 20 to 50 parts of titanium dioxide in the course of the aforementioned kneading a white-enhanced plate was obtained. A similar effect was brought about with each of the compounds of Examples 6 to 16. Further, a similar white-enhancing effect was also imparted to polymethyl methacrylate resin, polyvinylchloride resin, polyamide resin, polyester resin, and polycarbonate resin, when used in place of polystyrene resin in this Example.

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## WHAT WE CLAIM IS:—

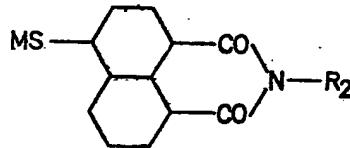
1. A naphthalimide derivative having the following formula (1):



5 wherein R<sub>1</sub> denotes an unsubstituted or substituted alkyl, aryl, aralkyl or cycloalkyl group having no dyestuff character and R<sub>2</sub> denotes a hydrogen atom or an unsubstituted or substituted alkyl, aryl, aralkyl or cycloalkyl group having no dyestuff character.

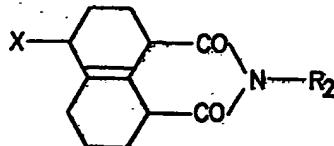
2. N-alkyl-4-alkylthio-naphthalimides.
3. N-methyl-4-n-butylthio-naphthalimide.
4. N-methyl-4-methylthio-naphthalimide.
5. N-n-butyl-4-methylthio-naphthalimide.
6. N-hydroxyalkyl-4-alkylthio-naphthalimides.
7. N-(2'-hydroethyl)-4-methylthio-naphthalimide.
8. 4-alkylthio-naphthalimides.
9. 4-methylthio-naphthalimide.
10. N-(N',N'-dialkylaminoalkyl)-4-alkylthio-naphthalimides.
11. N-(N',N'-dimethylaminopropyl)-4-methylthio-naphthalimide.
12. N-aryl-4-alkylthio-naphthalimides.
13. N-phenyl-4-methylthio-naphthalimide.
14. N-alkyl-4-hydroxyalkylthio-naphthalimides.
15. N-methyl-4-(2'-hydroxyethylthio)-naphthalimide.
16. N-alkyl-4-(N',N'-dialkylaminoalkylthio)-naphthalimides.
17. N-methyl-4-(N',N'-dimethylaminoethylthio)-naphthalimide.
18. N-alkyl-4-arylmethylthio-naphthalimides.
19. N-methyl-4-benzylthio-naphthalimide.
20. N-methyl-4-(4'-nitrophenyl)thio-naphthalimide.
21. bis [4-(N-methyl naphthalimide)] sulphide.

25 22. A method of manufacturing a naphthalimide derivative as claimed in claim 1, which comprises etherifying a compound having the following formula (2):



30 wherein M denotes a hydrogen atom or an alkali metal and R<sub>2</sub> is of the same significance as in formula (1), by reacting it with an etherifying agent to produce the naphthalimide derivative as shown by the formula (1).

35 23. A method as claimed in claim 22, in which the compound having formula (2) is one manufactured by reacting a 4-halogeno-naphthalimide having formula (3):



wherein X denotes a halogen atom, with an alkali metal sulphide having the formula M<sub>y</sub> Sy, wherein M denotes an alkali metal and y a number from 1 to 5.

24. A method as claimed in claim 22, in which the etherifying agent is an ester of a strong acid, or an organic compound containing an active halogen atom or an ester of an organic sulphonate acid.

5 25. A method of optically whitening synthetic organic material of high molecular weight, which comprises treating the said material with a compound claimed in any one of claims 1 to 21. 5

10 26. A method as claimed in claim 25, in which the compound is fixed on or mingled with the said material during the course of either the manufacture or the fabrication of the material. 10

15 27. A method as claimed in claim 25, in which the said material is in the form of textile material and is treated with the compound in an aqueous medium. 15

28. A method of optically brightening a solid, synthetic organic polymer, substantially as hereinbefore described in any one of Examples 17 to 22.

29. A method for the manufacture of a naphthalimide of the formula given in claim 1, substantially as hereinbefore described with reference to any one of Examples 4 to 16.

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